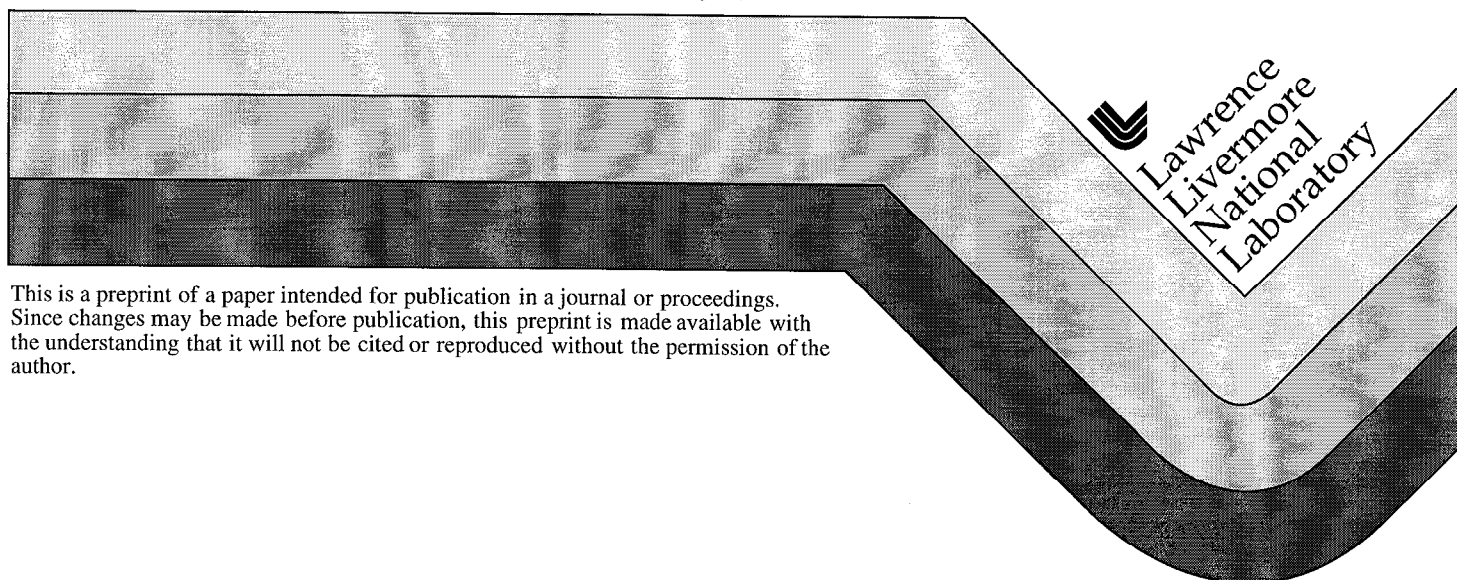


# Modeling High-Pressure and High-Temperature Phase Changes in Bulk Carbon

F.H. Ree  
J.N. Glosli

This paper was prepared for submittal to the  
*American Physical Society*  
*11th Topical Conference on Shock Compression of Condensed Matter*  
*Snowbird, UT*  
*June 27-July 2, 1999*

July 1, 1999



This is a preprint of a paper intended for publication in a journal or proceedings.  
Since changes may be made before publication, this preprint is made available with  
the understanding that it will not be cited or reproduced without the permission of the  
author.

#### DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

# MODELING HIGH-PRESSURE AND HIGH-TEMPERATURE PHASE CHANGES IN BULK CARBON

Francis H. Ree and James N. Glosli

Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, CA 94550

**Abstract.** The phase diagram of carbon is not experimentally well known at high pressure and/or high temperature. We have determined the phase diagram of carbon by means of Monte Carlo and molecular dynamics simulation methods using the Brenner bond order potential. The melting line of diamond was found to have a positive slope with the graphite-diamond-liquid triple point in agreement with an estimated value based on experiment. The present calculation predicts a first-order phase transition in liquid carbon terminated by a critical point and by a triple point on the graphite melting line. The low-density liquid is predominantly  $sp$  bonded with little  $sp^3$  character. The high-density liquid is mostly  $sp^3$  bonded with little  $sp$  character.

## INTRODUCTION

A typical HE molecule consists of C, H, N, and O atoms. A carbon-rich class of high explosives (HEs) is different from others whose thermochemistry is dominated by gaseous chemical reactions. Because gaseous reactions are generally very fast at temperature ( $T$ ) and pressures ( $P$ ) of interest, an assumption of thermochemical equilibrium results in reliable prediction of the HE performance for the second class of HEs.

In contrast, carbon-rich HEs require a consideration of carbon condensation reactions, which can take often longer than the time scale of a typical detonation experiment. In addition, modeling of the post-detonation behavior of carbon-rich HEs requires reliable equation of state (EOS) of carbon in bulk size as well as the EOS of small clusters and also the kinetics of carbon coagulation kinetics. This paper is mainly concerned with the EOS aspect of bulk carbon.

## MELTING LINE OF DIAMOND

We employ below a physically reasonable carbon-carbon potential developed by Brenner [1]

in molecular dynamics (MD) and Monte Carlo (MC) simulations to derive the melting line of diamond, of which all that is known is that it has a positive slope. Brenner's bond-order potential  $\Psi$  is given by

$$\Psi = \sum_{i,j \geq 1} [\phi^R(r_{ij}) - b_{ij} \phi^A(r_{ij})], \quad (1)$$

where the first and second terms represent repulsive and attractive contributions. The so-called bond order factor  $b_{ij}$  is a many-body term, which depends on bond angles, torsional angles, bond lengths, and atomic coordination in the vicinity of the bond. This many-body nature of  $b_{ij}$  makes the bond energy dependent on the local environment surrounding the bond. It allows the Brenner potential to predict correct geometry and energy for many different covalently-bonded carbon structures.

The diamond melting line can be determined by comparing the free energies of the diamond and the liquid phases. Briefly, we relate the reduced Helmholtz free energy,  $Q = A/kT$ , at volume  $V$  and  $\beta (=1/kT)$  to those at the reference state ( $V_0, \beta_0$ ) by

$$Q(V, \beta) = Q(V_0, \beta_0) + \int_{(V_0, \beta_0)}^{(V, \beta)} (\nabla Q) \cdot d\Gamma, \quad (2)$$

where MD simulations provide information on  $\nabla Q = \left( \frac{\partial Q}{\partial V}, \frac{\partial Q}{\partial \beta} \right) = (-\beta P, E)$  along a path  $\Gamma$  which is a path in  $(V, \beta)$  space connecting a reference state  $(V_0, \beta_0)$  to  $(V, \beta)$ .

The main task is to evaluate the free energy at  $Q(V_0, \beta_0)$ . For the liquid phase, we choose a finite temperature reference state and connect it to the ideal-gas limit by

$$\begin{aligned} Q_{liquid}^{ref} &= Q_{liquid}(V_0, \beta_0) \\ &= Q_{ideal}(V_0) + \int_0^{\beta_0} E d\beta, \end{aligned} \quad (3)$$

where  $Q_{ideal} = -N \log(V) + \log(N!)$ . For diamond phase, we determine the free energy  $Q_{solid}^{ref}$  of the reference state using an artificial path between the system with potential energy  $U$  and a model system with potential energy  $U_m$  and a free energy  $Q_m$ .

Now define a new potential energy function  $\hat{U}(\gamma) = (1-\gamma)U_m + \gamma U$ . By varying a coupling constant  $\gamma$  from zero to one, one can derive a relation,

$$\begin{aligned} Q_{solid}^{ref} &= Q_{solid}(V_0, \beta_0) = Q_m(V_0, \beta_0) \\ &+ \beta_0 \int_0^1 d\gamma < U - U_m >_{\gamma} \end{aligned} \quad (4)$$

For the model system we use a non-interacting harmonic crystal with an analytic expression for its free energy. We use a common reference state for both liquid and solid, i.e., at  $V_0 = (1.5 \text{ \AA})^3$  and  $T_0 = 5,000 \text{ K}$ , where we use the MC and MD simulations to evaluate  $E$  in Eq. (3) and  $< U - U_m >_{\gamma}$  in Eq. (4), as explained in Ref. [2]. Results are:

$$\begin{aligned} \text{liquid: } Q_{liquid}^{ref} / N &= -13.224 \pm 0.002 \\ \text{solid: } Q_{solid}^{ref} / N &= -13.1361 \pm 0.0005. \end{aligned}$$

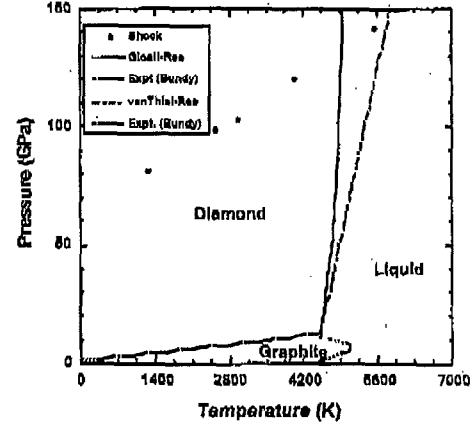


FIGURE 1. Theoretical and experimental phase diagrams of carbon: Shaner et al.'s shock sound-speed data from Ref. [5], diamond melting line from Ree-Glosli from Ref. [2] and van Thiel and Ree [4], experimental graphite-diamond and graphite-melt lines by Bundy in Ref. [3].

The resulting melting line is displayed in Fig. 1 along with experimental graphite-diamond and graphite-liquid phase boundaries [3]. Semi-empirical diamond-melting line of van Thiel and Ree [4]. The present melting line agrees remarkably well with experiment near the graphite-diamond-liquid triple point. The slope of the melting line is positive, which is also consistent with Shaner et al.'s sound speed data [5] (plotted against their estimated temperature) along the Hugoniot except at their high-pressure end.

## TWO TYPES OF LIQUID CARBON AND THEIR STRUCTURES

Togaya's recent flash-heating experiment [6] gave a strong indication that the slope of the melting line changes its sign at about 5.6 GPa, suggesting a presence of a first-order phase change in liquid carbon. His experiment reinforces our earlier prediction [7] that liquid carbon may exhibit two phases, separated by a first-order phase change.

We performed MD simulations with 512 carbon atoms interacting with the Brenner potential to test such a possibility [8]. Figure 2 confirms this prediction. We note that pressure isotherms show classic van der Waals loops associated with a first-order phase transformation. We determined the phase coexistence region between the high-density

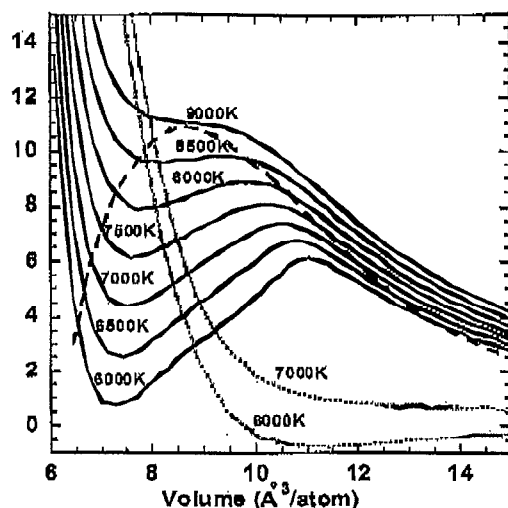


FIGURE 2. Isotherms (solid lines) and liquid-liquid phase boundaries (dashed line) based on Brenner's bond-order potential from Ref. [8]. Dotted line = isotherms without the torsional energy term.

liquid (HDL) and the low-density liquid (LDL), and the corresponding  $P$ - $T$  phase line by the equal-area construction on the van der Waals loop. These are shown in Figs. 2 and 3, respectively.

We can estimate the locations of the graphite-melting line. The resulting liquid-liquid phase line terminates at a critical point (8801K, 10.56 GPa) and a graphite-liquid-liquid (GLL) triple point on the graphite melting line at (5133K, 1.88 GPa). Slopes of the graphite-HDL, graphite-LDL, and HDL-LDL lines are -0.0189, 0.00585, and 0.00224 GPa/K, respectively.

One measure of liquid structure is the local coordination of each atom. The present simulation shows that the four-fold coordinated atoms are the centers of nearly tetrahedral structures, and that the three-fold coordinated atoms are the centers of planar structures with the neighbors at angles close to  $120^\circ$  and the two-fold coordinated tend to be linear. So two-, three-, and four-fold coordinated atoms will be  $sp$ ,  $sp^2$ , and  $sp^3$  hybridized, respectively.

We find that the HDL is mostly four-fold coordinated or  $sp^3$ -like and that the HDL has mostly two-fold coordination or  $sp$ -character with only

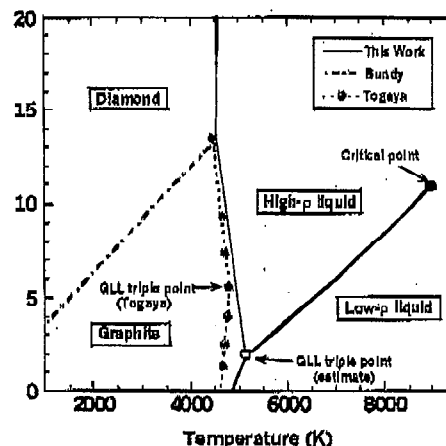


FIGURE 3. Phase diagrams of carbon based Brenner's bond-order potential Ref. [8]. Gray circles = experiment Ref. [6]

small amounts of three-fold coordination or  $sp^2$ -character.

## DISCUSSIONS

At low  $P$  the LDL is dominant because the linear chain structures are stabilized over  $sp^2$  or  $sp^3$  structures by entropy. At higher  $P$  the  $\sigma$  bond in the  $sp^3$ -liquid allows for almost free rotations about the bond of the local tetrahedrals leading to many nearly equal energy conformations and high entropy. In contrast,  $\sigma\pi$  bond in the  $sp^2$ -liquid has a large torsional energy barrier, and it forces the structure to be planar, and of much lower entropy than the  $sp^3$  dominated phase. This low entropy destabilizes the  $sp^2$ -liquid phase relative to the  $sp$ - or  $sp^3$ -liquid phases. The role of the torsional energy in the liquid is illustrated in Fig. 2. Without torsional term (dotted lines), the van der Waals loop vanishes at 7000K and is greatly reduced at 6000K over the isotherm corresponding isotherm of the full potential model. It clearly shows the importance of the  $\sigma\pi$  bond's torsional energy.

The above calculation of the melting line was done with the Brenner potential which represents only the covalent-bonding with a short-range cutoff. We need to modify it to include the long-range van der Waals non-bonded term to hold two-dimensional graphite sheets together. This work is in progress. The LDL phase is particularly sensitive

to the van der Waals forces. The inclusion of these forces ought to significantly increase the density of the LDL phase at a given pressure. This change would increase the transition pressure to the HDL phase, bringing such refined calculations in closer agreement with Togaya's experiment.

It is important to validate experimentally the predicted first-order phase change in liquid carbon. One suggestion is to perform a shock wave experiment with a low-density aerogel of carbon. Carbon-rich foam is soft. If shocked, it can attain an enormous compression and high shock heating at low shock pressure. Hence, it is an ideal sample to explore a pressure-temperature range of interest. Shon et al. made such calculations to give a theoretical guidance to provide a possible initial and final shock conditions necessary to detect the predicted phase change [9]. Their calculations predict that Hugoniot experiments with an initial density of  $0.15 \text{ gm/cm}^3$  has the best chance for observing liquid-liquid phase transition.

#### ACKNOWLEDGMENTS

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

#### REFERENCES

1. Brenner, D. B, *Phys. Rev. B* **42**, 9458 (1990).
2. Glosli, J. N. and Ree, F. H., *J. Chem. Phys.* **110**, 441 (1999).
3. F. P. Bundy, *J. Chem. Phys.* **38**, 618 and 631 (1963).
4. Van Thiel, M. and Ree, F. H., *Int. J. of Thermophys.* **10**, 227 (1989).
5. J.W. Shaner, J.M. Brown, C.A. Swenson and R.G. McQueen, *J. Phys.* **45**, 235 (1994).
6. Togaya, M., *Phys. Rev. Lett.* **79**, 2474 (1997).
7. Van Thiel, M. and Ree, F. H., *Phys. Rev. B* **48**, 3591 (1993).
8. Glosli, J. N. and Ree, F. H., *Phys. Rev. Lett.* **82**, 4659 (1999).
9. J. Shon, et al., see this Proceedings.